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Re: NREL Subcontract #ADJ-1-30630-12

Dear Ken:

This report covers research conducted at the Institute of Energy Conversion (IEC) for the period
from October 9, 2005 to November 9, 2005, under the subject subcontract. The report highlights
progress and results obtained under Task 1 (CdTe-based solar cells).

TASK 1 – CdTe-BASED SOLAR CELLS

Alternative Cu-based contact processing for CdTe/CdS devices

In a recent review, we discussed a number of different modes of delivery of Cu during back
contacting of CdTe/CdS devices.[1] One of the applications discussed was spray coating of Cu-
salt solutions. This approach offers a number of possible benefits, including: i) it is a simple and
fast application of contacting material, ii) allows easy variation of solution and contacting
conditions, and iii) allows easy testing of different contacting metals. It is also an industrially
mature and significant process. We have carried out a series of experiments to test the viability
and optimize this approach for CdTe/CdS device processing.

All devices were processed with 5 μm CdTe substrates, which had received $CdCl_2$ treatment.
Prior to spray contacting, substrates were etched with either Br_2/methanol, generally 0.05% for
10 sec, or with the aniline-based surface treatment, generally 60 min under illumination. For
spray contacting, a range of Cu salts were selected for testing; including CuCl, CuBr and CuI.
Generally, methanol solutions were prepared at concentrations of $10^{-3} – 10^{-4}$ M, though this was
dependent on the solubility of salt. Contacting with saturated CuI/methanol solutions, which
have a concentration of $\sim 2 \times 10^{-4}$ M CuI, was found to produce the best devices by this method. A
nasal spray bottle, which delivers ~0.03 mL per spray, was used to apply the solution onto a
warm CdTe substrate. Only a few sprays were applied at a time, allowing the solvent to
evaporate before continuing. The effects of 10-50 sprays on device performance were evaluated,
with 15-20 sprays being found to be optimal. Following spray contacting, devices were
completed with graphite paste and received anneal treatment at 180-200°C for 15-20 min.

As stated above, 10-20 sprays of CuI was found to produce the best devices, with V_{oc} =790-810 eff.>10% and >11% for Br_2/methanol and aniline etching, respectively. Applying fewer or more sprays resulted in a decrease in device quality, indicating the sensitivity of the devices to the levels of Cu delivered. Devices contacted with CuCl and CuBr salts tended to be slightly poorer in performance than CuI contacted devices, suggesting that the anion species has a controlling role in the back contact formation reaction. Attempts to compare other Cu salts, including Cu(acetate), CuSCN and CuCN, were hampered by their very low solubility in methanol. Attempts to vary the solvent to improve salt solubility were not successful. For example, acetonitrile was found to evaporate too readily and could not guarantee a uniform coverage of the surface. Methanol appears to be the most useful solvent for this approach due to its slower rate of evaporation and low cost.

The effects of varying the Cu concentration were monitored using CuCl/methanol solutions. CuI was not investigated due to its lower solubility in methanol. Devices were contacted with 10 sprays of solutions of $2x10^{-4}$, $1x10^{-3}$ or $5x10^{-3}$ M CuCl in methanol. The devices with the two lower concentrations exhibited similar behavior, with Eff. = 9.0 and 9.2%, respectively, and V_{oc}~800 mV. The higher concentration device, however, showed a significant decrease in performance, with V_{oc} ~ 630 mV and eff. = 6.3%. This again indicates the sensitivity of the devices to the amount of Cu delivered during processing.

The use of hydrated salts, even at concentrations as low as ~10^{-4} M, was found to be detrimental to device performance. The water present in the salts inhibits the contact chemistry, most likely by oxidizing the Te-rich surface or the Cu ions and preventing formation of a favorable back contact. Therefore, only anhydrous salts should be used.

We have also evaluated other metal salts, including $CuCl_2$, $ZnCl_2$, ZnI_2, $NiCl_2$ and NiI_2 for contacting CdTe. Methanol solutions at concentrations of 10^{-3} and $2x10^{-4}$ M were used. As we have reported in the past,[1] Cu^{2+} salts generally produce poorer back contacts than Cu^+ salts to CdTe, which we observed with this approach; though using lower anhydrous $CuCl_2$ concentrations ($2x10^{-4}$ M) did result in devices approaching 9% efficiency with V_{oc} ~700-750. Both of the Ni salts, at each concentration, generally produced devices of around 7-8% efficiency with V_{oc} of 700-760mV. The Zn salts showed promising behavior, with 10^{-3}M $ZnCl_2$ producing devices with V_{oc}~800 mV and eff.>9%, and 10^{-3}M ZnI_2 producing devices of V_{oc} of 770-800mV with efficiency 10.2-10.5%. Further investigation of the ZnI_2 salt is underway, as well as, further exploration of other potential metal salts for CdTe back contacting.

We have shown the spray method of contacting CdTe devices to be a very successful and industrially significant approach. Contacting can be carried out very quickly and easily, and allows for the simple testing of different metal salts and different contacting conditions. This approach is now often used for contacting devices in our laboratory.

Back contact analysis using bifacial CdTe devices

With a Cu-doped ZnTe semi-transparent back contact, junction and transport properties can be determined by applying bifacial characterization techniques [2,3] to CdS/CdTe solar cells. For front illumination, though CdS, most of the light is absorbed in the depletion region and the back junction is nominally in the dark. In contrast, for back illumination, most of the light is absorbed in the field free region and minority carriers (electrons in p-type CdTe) must diffuse to the depletion edge of the front junction. In CdS/CdTe solar cells, the back contact presents a barrier to hole injection and may induce a field ,which could affect overall device operation as the absorber thickness is reduced. A bifacial device provides a tool to study photocurrent collection and back contact behavior previously unavailable with front illumination.

ZnTe:Cu films were grown on glass/SnO$_2$/CdS/CdTe substrates. The CdTe was 1.5, 2.5, 5 and 10 μm thick and was deposited at 550°C by vapor transport (VT) at the IEC. The CdTe surface was first treated by one of three processes to remove any oxide present and create a Te rich surface: the 3 step BDH process (Bromine-methanol, then Dichromate, then Hydrazine), aniline, or Br-methanol. Sputtered ITO and evaporated Ni/Al grids were used as secondary back contacts. Table I lists the device parameters for two different CdTe surface treatments for VT178 (5 μm). Performance is similar between the two surface treatments.

Table I. Device results for devices from 2 VT runs made with ZnTe:Cu contact for front wall or back wall light with aniline, or Br-Methanol surface treatment.

Contact (Sample#)	CdTe Surface treatment	Light direction	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	Eff (%)
ZnTe (VT 178.5)	Aniline	Front	814	22.2	68	12.3
		Back	677	1.2	70	0.5
ZnTe (VT178.2)	Br-Meth	Front	804	22.4	67	12.1
		Back	672	1.5	67	0.7

The J(V) curves for CdTe devices often show light-to-dark crossover (LDXO) at forward bias attributed to Cu-doped photoconductive CdS, or they show roll-over (curvature) attributed to blocking contacts. Figure 2 shows the J (V) curves for the two devices from Table I. They are typical of a larger number of pieces, we have processed. Namely, devices receiving the aniline (or BDH, not shown) treatment prior to ZnTe:Cu growth typically have no rollover and very slight LDXO. Devices receiving BR-methanol typically have significant rollover in forward bias, indicating a higher barrier. Yet Table I showed that the solar cell performance was not strongly affected. The penetrating nature of the BDH treatment results in shorted devices when the CdTe is less than 5 μm. Therefore, subsequent processing of these cells with ZnTe:Cu will use the aniline treatment, since it results in ohmic contacts and high yields in thin devices. Another factor requiring optimization is the post-contact heat treatment, typically at 180°C for 30 min.

A crucial new result is shown in Figure 1 for VT178-2 (Br-Me etch, right). Roll-over occurs in forward bias for light through the front or in the dark *but not for light through the ZnTe:Cu.* We have observed this on several other pieces from other CdTe runs and with different CdTe thickness and different surface etch chemistry/processing and after stress (i.e. VT154-4 in Figure 2). Due to the high absorption of CdTe, the back contact is in the dark for front illumination and for wavelengths < 850 nm. However, the JV curve for the back illumination rises without curvature and has lower resistance. This demonstrates the photo-sensitivity of the back contact; i.e. either the ZnTe:Cu or the contact/junction region are photoconductive and create a blocking contact unless illuminated for light with $h\upsilon > 1.4$ eV. It is consistent with re-contacting studies reported by IEC where replacing the graphite back contact eliminated the rollover, which developed after stressing but had no effect on V_{oc} or FF. There was no blocking contact for VT154-4 before stress. Clearly stress increased the barrier of the back contact as seen in Figure 2.
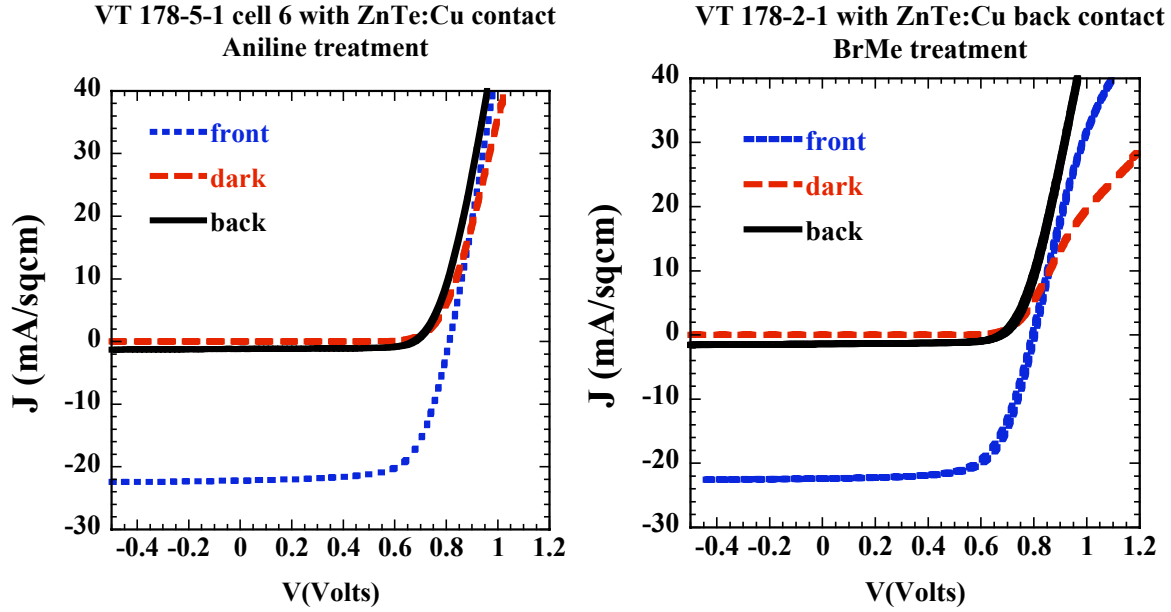

Figure 1. Initial J(V) curves for devices from Table I with ZnTe:Cu contacts with aniline (left) or Br-Me (right) for illumination through CdS (front), ZnTe:Cu (back) and dark.

VT154.4-2 with ZnTe:Cu contact
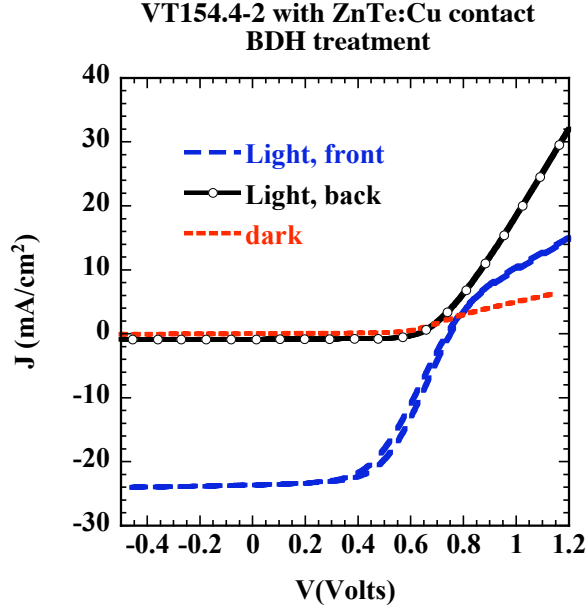**BDH treatment**

Figure 2. J(V) curve after 10 days stress at 100°C, OC for VT154-4 with ZnTe:Cu contacts for illumination through CdS (front), ZnTe:Cu (back) and dark. A blocking contact disappears when the cell is illuminated through the back contact.

Bifacial Spectral Response Characterization: effect of CdTe thickness

A model had been developed previously for bifacial spectral analysis of transparent contact for CIS based photovoltaic devices.[2] This model evaluates the spectral response as a function of absorber thickness (t), depletion width (W) and diffusion length (L). We have applied this to CdS/CdTe devices with ZnTe:Cu back contacts.[3] Due to the extremely high CdTe absorption coefficient and steep absorption edge, over 90% of the photocurrent is generated within 2 μm for either illumination direction. For standard front wall measurements, through CdS, the light is absorbed in the high field depletion region leading to very high collection probability independent of t, W or L, providing that t and W exceed ~2 μm. In contrast, the back wall spectral response measurements are much more sensitive to L and W than front wall spectral response since the back wall region is not expected to have a high field.

Figure 3 shows the back wall SR measured at –0.8V, 0V and +0.5V on VT178-2-1 whose JV curves are in Figure 1. The fitted value is also shown along with values of W and L. For back wall measurements, most of the electrons generated in the CdTe bulk must diffuse to the junction depletion region and is represented by the increasing tail from 600 to 800 nm. Carriers generated in the depletion region by weakly absorbed near-bandgap light (800-860 nm) are collected with high probability, represented by the peak from 800-860 nm. Typically, we observed very little increase in front wall SR from zero to –1V bias, indicating good collection and consistent with the strong absorption in the depletion region.
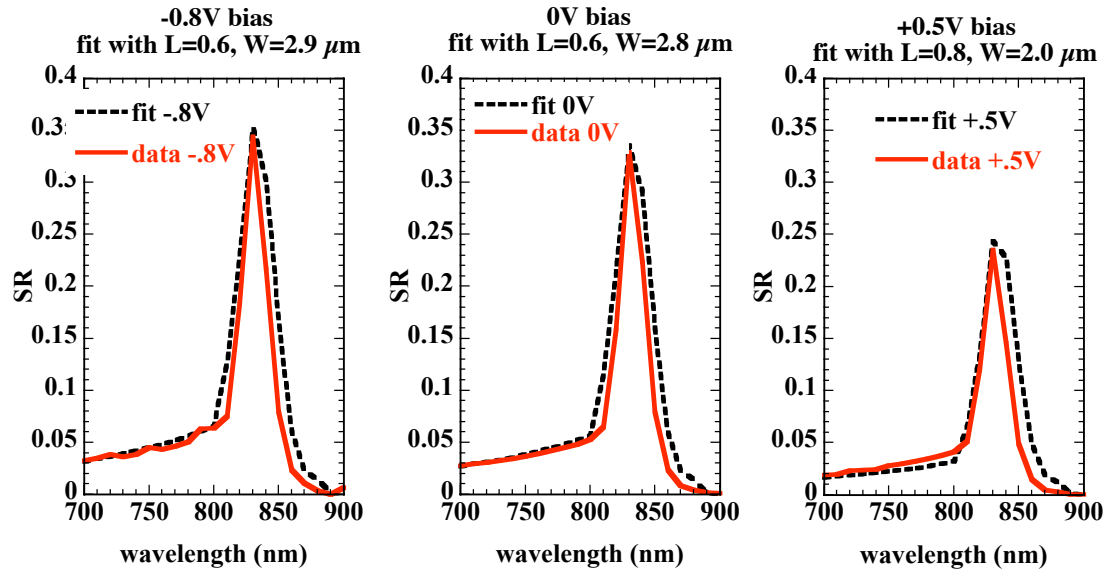
Figure 3 Back wall SR for VT178-2-1 (t=5 μm) at 3 voltage biases. Measured data and fit with L, W values indicated are shown.
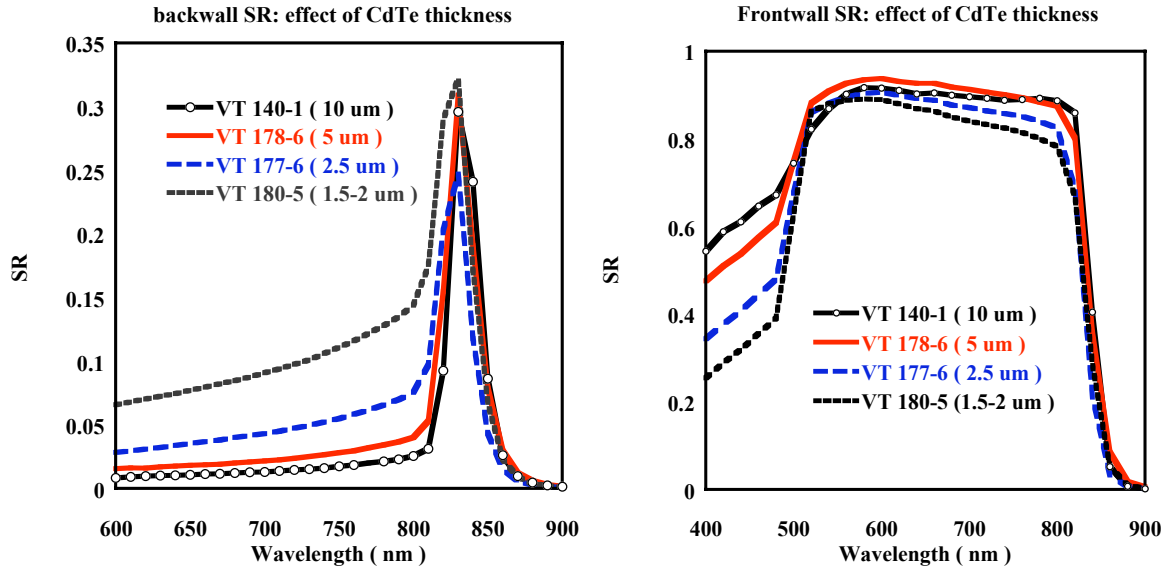

Figure 4 (left) shows the back wall SR and Figure 5 (right) shows front wall SR (right), each for 4 devices with different CdTe thickness.
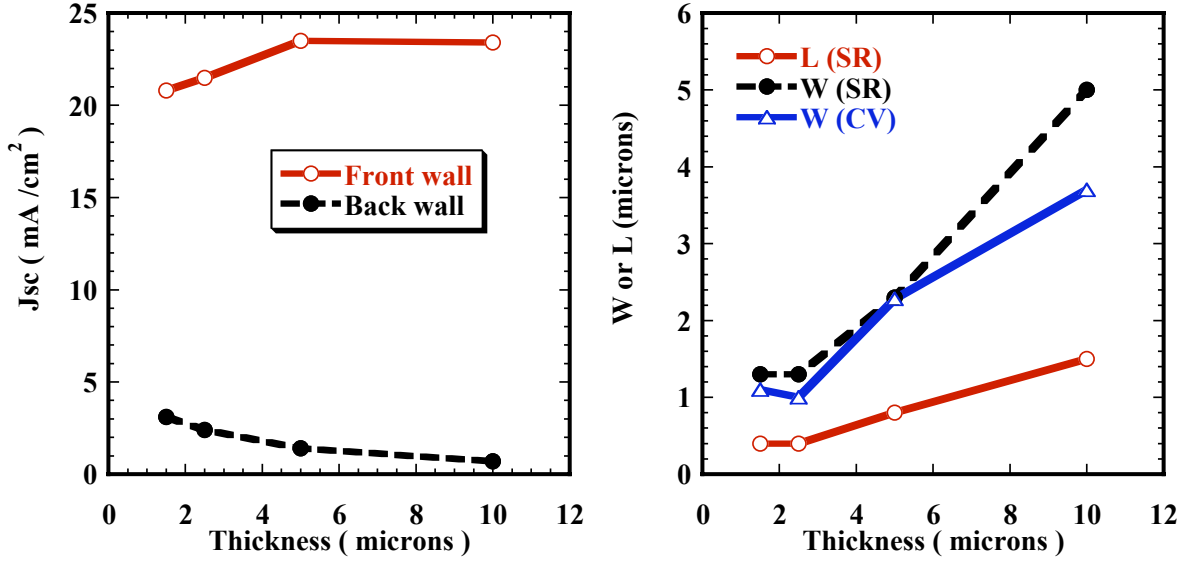
Figure 6 (left) shows the J_{sc} for FW and BW as a function of CdTe thickness. Figure 7 (right) shows the depletion width W at 0V and diffusion length resulting from fit to back wall SR and W at (0V) from CV.

Figure 4 shows the back wall SR for cells of 4 different CdTe thicknesses. As t increases, the neutral bulk region, t-W, increases, the distance carriers must diffuse increases, hence the SR of the diffusion tail (<800 nm) decreases. Figure 6 shows that the back J_{sc} decreases with increasing CdTe thickness in agreement with the SR data. Figure 6 also shows that the front J_{sc} increases with increasing thickness between 1.5-5 μm. However, the front QE in Figure 5 shows there are two separate effects occurring. The response below 520 nm is increasing significantly with increasing thickness, presumably due to a reduction in CdS-CdTe interdiffusion due to lower grain boundary density. The response beyond 600 nm is also decreasing slightly due to reduction in volume carrier generation. Without the difference in interdiffusion, the increase in front J_{sc} with thickness would be much smaller. Back wall collection is limited by diffusion through the bulk. Figure 7 shows W (0V) and L obtained from fitting the back wall SR. Both increase steadily with thickness. The increase of L with t suggests a decrease in defects with increasing thickness perhaps due to improved grain structure. Figure 7 also shows good agreement between W (0V) from SR fitting and CV measurements, confirming the validity of the SR model to the bifacial CdTe devices. This may be due to reduction in impurity diffusion from the rear contact. Future work will involve varying the Cu concentration in the ZnTe:Cu, the heat treatment, and performing accelerating stressing.

References

[1] B. E. McCandless and K. D. Dobson, Solar Energy, 77 (2004) 839.
[2] J. Phillips, Proc. 21th IEEE Photovoltaic Spec. Conf., 782 (1990).
[3] D. Desai, S. Hegedus, B. McCandless, D. Ryan, MRS Symp. Proc.865 (2005). Paper Number F14.9

Best regards,

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Director

RWB/bj

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